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Ithaca, N.Y.

May 1971

CRSR 445

ULTRAVIOLET SELECTION PRESSURE ON THE EARLIEST ORGANISMS

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Abstract

An examination of the probable photochemistry of the primitive reducing atmosphere of the Earth reveals a window, approximately bounded at 2400 Å to short wavelengths by H_2S, and possibly at 2700-2900 Å to longer wavelengths by aldehydes. The solar ultraviolet flux in this 2600 Å window, delivered to unprotected organisms at the surface, corresponds to a contemporary mean lethal dose in $\leq$ 0.3 seconds. Extreme selection pressure for ultraviolet protection must have come into being. In addition to the early evolution of pyrimidine dimer ligases, catalase and peroxidase reduction mechanisms, and photoreactivation, it is suggested that two evolutionary paths developed. In one, heterotrophs lived below the oceanic thermocline and are suggested as perhaps the ancestors of the prokaryotes. In the other, organisms living near the oceanic surface surrounded themselves with ultraviolet absorbing layers of purines and pyrimidines. The resulting organisms have dimensions of tens to hundreds of microns and are suggested to be the ancestors of the eukaryotes. Subsequent specialization of this initially inert shielding, e.g., into ribosomal RNA, may have occurred.

Some years ago I proposed that uv light, partially penetrating the primitive reducing atmosphere of the Earth, posed a major problem for the earliest evolution of life (1). This argument can now be updated and refined. We adopt the by now traditional picture of a secondary reducing atmosphere, from which an excess of hydrogen has already escaped to space, at a total surface pressure $\sim$ 1 bar. The predominant constituents, methane, ammonia, water vapor, CO, N_2, H_2, and the noble gases are all perfectly transparent for these pressures at wavelengths $\lambda \geq 2200$ Å. Hydrogen sulfide is another probably important constituent of the primitive terrestrial atmosphere: it is the thermodynamically stable sulfur-containing gas under reducing conditions, and is even today a volcanic effluent. Holland (2) estimates that the volume mixing ratio of H_2S in the first stage of the evolution of the Earth was between 10^{-2} and 10^{-4}; that is, $\sim 10^2$ to 10^4 cm-atm H_2S (1 cm-atm of gas = a columnar density of Loschmidt's number of molecules, 3×10^{19} molecules cm^{-2}). But this is an estimate made while ignoring photochemical degradation, which we know is very efficient; in fact the photolysis of H_2S may itself have played a very major role in the prebiological formation of organic compounds (3). From the laboratory absorption spectrum of H_2S (4), which shows the absorption coefficient to decline approximately 1 order of magnitude every 100 Å below 2400 Å, it appears likely that H_2S contributed negligible opacity on the primitive Earth at $\lambda >$ 2400 Å - 2600 Å (cf. Fig. 1).

Accordingly, a significant ultraviolet window appears to have existed at $\lambda \gtrsim 2400$ Å, tempered only by intermediate oxidation state products produced by the photochemistry of the principal constituents. By far the most abundant such absorbers are the aldehydes; formaldehyde and acetaldehyde have been detected in the gas phase in a number of simulation experiments (5). Indeed the aldehydes are known intermediaries in the prebiological organic synthesis of both sugars and amino acids. The ultraviolet absorption spectra (6) of formaldehyde and acetaldehyde are shown in Fig. 1. Between 2400 Å and 2900 Å the molar extinction coefficients have values of several dimensionless units, corresponding to a molecular cross-section σ of the order of 10^{-20} cm^2. Thus optical depths $\tau \sim 1$ are achieved with a columnar density of 10^{20} molecules cm^{-2}, which in turn corresponds to $\sim$ 3 cm-atm or $\sim$ 3 ppm. Models of solar evolution place the Sun about half a bolometric magnitude fainter 4×10^9 years ago than it is today; but the resulting uv flux can be calculated to be only slightly less than it is today (7). With such a flux, typical unprotected contemporary organisms -- both eucaryotes and procaryotes -- acquire a mean lethal dose [cf. ref. (8)] of ultraviolet radiation at $\lambda \leq 2900$ Å in ≤ 0.3 sec. Unacceptably high mutation rates will of course occur at much lower uv doses, and even if we imagine primitive organisms having much less stringent requirements on the fidelity of replication than do contemporary organisms, we must require very substantial uv attenuation for the early evolution of life to have occurred. This is especially true if we imagine

contemporary uv-protection mechanisms -- such as pyrimidine dimer ligases, photoreactivation, catalase, and the peroxidases -- to have been absent.

In the following discussion we assume that in some manner or other the incident uv flux between 2400 Å and 2900 Å had to be attenuated by a factor $\sim 10^9$, corresponding to $\tau \sim 20$. For $\tau \gtrsim 20$ to be provided by aldehydes, they must have constituted $\sim$ 100 ppm in the primitive atmosphere. Again, precisely because aldehydes absorb uv light so readily, they are irreversibly broken down into other photoproducts. From the aldehyde cross-sections of Fig. 1, it is easy to calculate that the mean lifetimes of such molecules in the primitive uv radiation field were a few hours. For an equilibrium abundance as high as 100 ppm, the production rate would have had to be $\sim 3 \times 10^{17}$ molecules cm^{-2} sec^{-1}, which appears to be excessive by a large factor. The situation is quite similar to the contemporary ozone photochemistry in the Earth's atmosphere, where the photochemical equilibrium abundance is only 10^{-1} to 10^{-2} ppm. However ozone absorbs much more strongly than the aldehydes in this wavelength region. Acetone and higher ketones have slightly larger absorption coefficients at $\lambda > 2400$ Å than do aldehydes (6), but their abundance in the primitive atmosphere should have been much smaller; indeed, to the best of my knowledge, they have never been reported in prebiological organic chemistry simulation experiments. Benzene and polycyclic aromatic hydrocarbons also absorb in the region of interest, but their gas phase abundance in the primitive atmosphere is expected to be

much smaller yet.

While it is clear that there remain many uncertainties about so remote a question as the composition of the primitive terrestrial atmosphere, it does appear that a significant window existed between 2400 Å and 2900 Å. Because of the shapes of the H_2S and aldehyde absorption spectra (see Fig. 1) the largest window appears to have been in the vicinity of 2600 Å. But this is precisely the vicinity of peak absorption by the nucleic acids. In the absence of repair the absorption of a single ultraviolet photon by the genetic material can be lethal. Repair mechanisms cannot be expected to have been as efficient in primitive times as they are today; and even today they are far from 100% efficient. Photoreactivation, for example, is ∿ 50% efficient. Thus the earliest self-replicating polynucleotides must have faced severe selection pressures to avoid uv damage. The development of enzymatic systems such as catalase and the peroxidases to undo uv-induced oxidations may have been developed very early (1); and the microbodies or peroxisomes of eucaryotes may date from very ancient times.

But in general there are only two efficient solutions to the primitive uv hazard: sequestering and shielding. Liquid water absorbs in the 2400 Å to 2900 Å region, but with quite low absorption coefficients. Several tens of meters of pure liquid water are required for significant attenuation of the incident ultraviolet flux, and I proposed that some of the earliest living systems may have developed entirely in the abyssal depths (1). Of course the primitive soup in which

the origin of life occurred was not pure liquid water, and many uv absorbers can be expected to have been present. High molecular weight uv- and visible-absorbing polymers, still unidentified in composition, are a pervasive component of experiments in prebiological organic chemistry [e.g., ref. (3)]. Thus, unprotected organisms could have developed much closer to the surface than tens of meters. But they then ran the risk of being carried, by slow oceanic convection, to the very tops of the oceanic surface where the uv dose becomes intolerably high. The great advantage of a depth of some tens of meters is that it begins to approach the oceanic thermocline, below which there is much less effective convective transport to the surface than from higher levels. We can imagine primitive anaerobic heterotrophs evolving in the abyssal depths, safely protected from the uv flux characteristic of the surface layers, and metabolizing the variety of organic compounds produced higher up and carried by convection and molecular and eddy diffusion to their depth. I propose that these simple abyssal organisms were the precursors of the prokaryotes.

On the other hand the supply of abiogenic food-stuffs (and visible light) must have been very much larger near the surface, and an organism adequately shielded from the intense uv flux would have discovered a very rich and untenanted ecological niche there. The most suitable shielding material would seem to have been purine and pyrimidine bases -- the very source of the uv lability of nucleic acids. These materials have extremely high absorption coefficients between

2400 Å and 2900 Å and are known to have been produced efficiently in the early history of the Earth (9). I propose that another solution to the uv selection pressure was for the genetic material to surround itself with bases or nucleotides having no function whatever in replication or protein synthesis. Typical molar extinction coefficients for purines and pyrimidines, for nucleotides, and for the nucleic acids themselves are 6 to 8 x 10^4, corresponding to $\sigma \simeq 3 \times 10^{-16}$ cm^2 (10), a very high value. An equimolar mixture of the five biologically most common purines and pyrimidines produces an approximately flat net absorption spectrum between 2400 Å and 2900 Å. Considering the crudeness of this calculation we neglect all hypochromic and solvent effects; they vary the absorption coefficient characteristically by ~ 50%. The aromatic and heterocyclic amino acids also absorb in this region and might have played a protective function; but their molar extinction coefficients are less than the purines and pyrimidines by factors of about 30; and the laboratory experience in prebiological organic chemistry indicates that tryptophan, e.g., is made much less abundantly than adenine. We assume that a few percent of the total weight of the shielded cell was in polynucleotide shielding; this is roughly the same value as the fractional weight of RNA in both procaryotic and eucaryotic cells (11). If the shielding comprised several tens of percent by mass, correspondingly smaller cells are implied. It is then easy to calculate that a cell so protected would have to be roughly 20 μ in radius to achieve $\tau = 1$, and 400 μ in radius to

achieve $\tau = 20$, in the absence of any atmospheric or solution shielding. But the characteristic dimensions of the simplest eukaryotes, the higher protists, are also between a few μ and a few hundred μ (12). I therefore suggest that while the prokaryotes developed at abyssal depths, the eukaryotes developed, at a somewhat later time, near the surface of the waters and with an ultraviolet umbrella of purines and pyrimidines. A number of the differences between prokaryotes and eukaryotes are consistent with this picture; for example, the eukaryotic genetic material is carefully maintained within the nuclear membrane and near the center or most uv-inaccessible region of the cell; prokaryotes, which in any case fall short by several orders of magnitude in meeting our protection criterion, appear to have their DNA strands anchored near the periphery on the cell membrane (13). Contemporary eukaryotes are probably not much better shielded from uv than are contemporary prokaryotes; nor are their nuclei surrounded by layers of passively functioning purines and pyrimidines and their compounds. But a great deal of evolution has obviously occurred since the earliest times we are discussing, and it is even possible that cytoplasmic nucleic acids, which originally played a protective role, eventually developed under the action of uv into performing other functions, including the ribosomal apparatus (14). The fact (15) that major fractions of the ribosomal RNA can be enzymatically digested away without significantly impairing ribosomal function suggests that ribosomal RNA may be an evolutionary relic from times when it played other functions. Otherwise we could

imagine ribosomal proteins rather than RNA providing all the structural links between enzymatically active ribosomal sites. The very early evolutionary path proposed here is not necessarily inconsistent with the idea of a prokaryote endosymbiont origin of eukaryotes (16); the abyssal and surface populations could not but have maintained genetic content.

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(17) This research was supported in part by NASA Grant NGR 33-010-101. I am indebted to Paul Shapshak for several stimulating discussions, and to K. C. Atwood and Leslie Orgel for helpful criticism.

Figure 1. Ultraviolet absorption cross-sections as a function of wavelength for H_2S and the two simplest aldehydes. For reasonable abundances of these gases in the primitive atmosphere, a significant 2400 Å - 2700 Å ultraviolet window is implied.

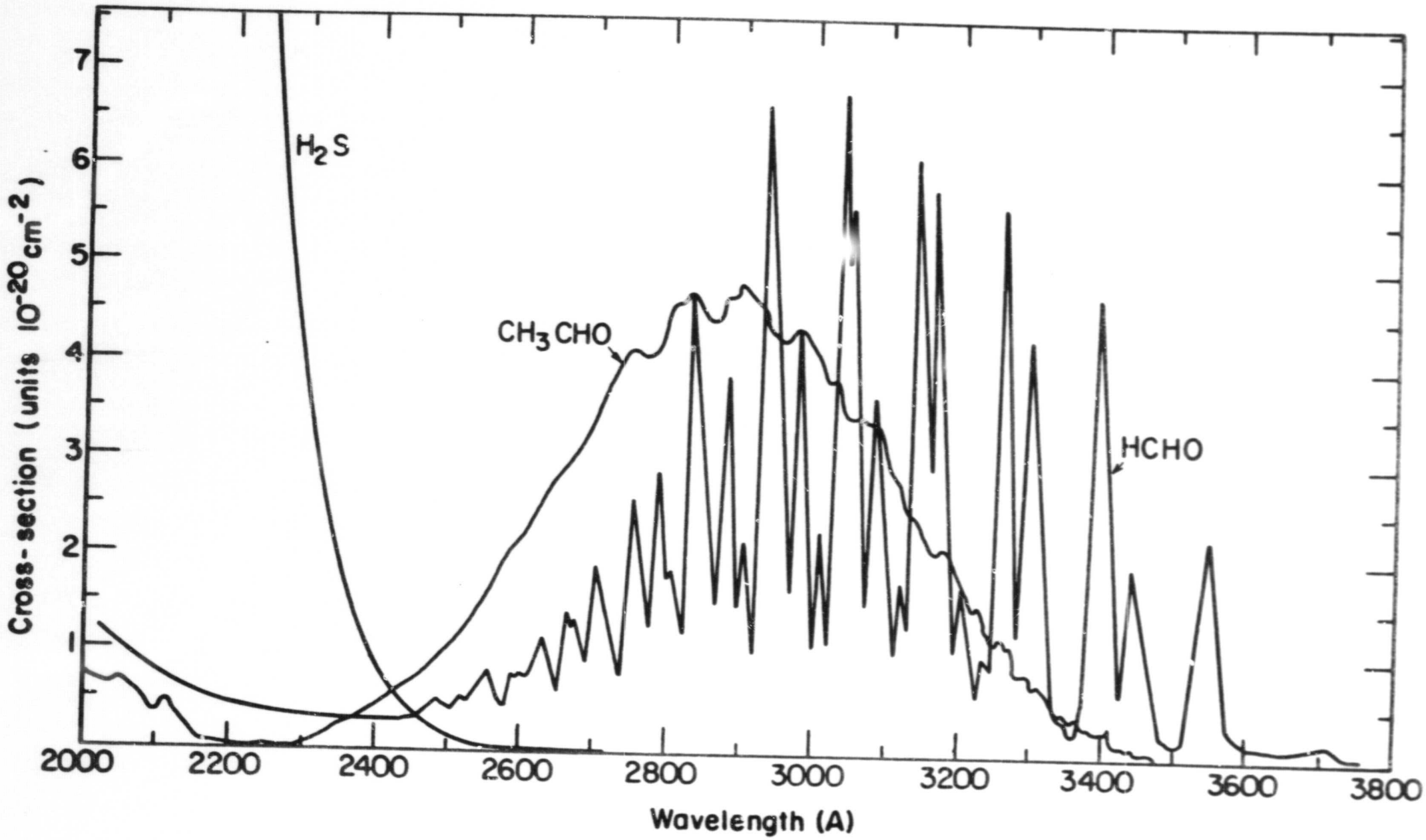
H_2S
CH_3CHO
HCHO
Cross-section (units $10^{-20}cm^{-2}$)
1
2
3
4
5
6
7
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
Wavelength (A)

Figure 1.